

## LAID-OPEN PATENT GAZETTE

Laid-Open No. 1987-83311

Laid-Open Date: April 16, 1987

Examination: Unrequested

Title: A method of producing a gel and a molded product

Application No. 1985-221906

Filing Date: October 7, 1985

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Claim

A method of producing a gel or a molded product from water (aqueous) silica sol or a slurry consisting of water silica sol and a granular material, comprising the step of controlling the ratio of the added quantity of at least one of the salts produced by reaction between strong bases and strong acids to the added quantity of at least one of the salts produced by reaction between strong bases and weak acids, and also the total quantity of the salts used, for keeping the water silica sol or the slurry consisting of water silica sol and a granular material flowable for a certain period of time and then quickly causing it to be thickened and gelled.

### Detailed description of the invention

The present invention relates to a method of gelling water (aqueous) silica sol, and a method of molding a slurry consisting of water silica sol and a granular material. Water silica sol is a colloid solution in which very fine grains of silica ( $\text{SiO}_2$ ) have been dispersed in water. The colloid grains have been covered, on the surface, with active silanol groups, and the water silica sol forms a stable sol because sodium ions ( $\text{Na}^+$ ), etc. prevent the mutual collision and deposition of the grains. The water silica sol has been being used in diverse industrial fields such as fibers, iron & steel, casting, forging, catalysts, refractories, electronics, etc. Especially, it has been being used as a binder for binding casting sand, refractory sand and other granular materials in the fields of casting, refractories, catalysts, etc., and the present invention provides a method of producing a gel and a molded product to be used in these fields by a new method.

#### [Prior arts]

It is extensively known that water silica sol can be instantaneously obtained by adding a metal salt aqueous-solution. However, it has not been being done that a slurry consisting of water silica sol and a granular material is kept flowable for a certain desired period of time after adding a gelling agent and then quickly thickened and gelled, to produce a molded product. Referring to the conventional (prior) method of quickly gelling a flowable slurry after a desired period of time for producing a molded product, the nature that alcoholic silica sol produced by hydrolysing an alkyl (e.g. ethyl) silicate in the presence of an acid catalyst is quickly gelled by the change of pH has been being used, as

used in the Shaw process and the uni-cast method widely known by Japanese Patent Publication Nos. 58-8264 and 76-32579, etc.

[Problems to be solved by the invention]

In the workshops where alcoholic silica sol is used in a large quantity, the acid as the catalyst and the alcohol as the solvent pollute the working environment, thus being unpreferable for the health and sanitation of workers and for the maintenance of apparatuses because they corrode jigs, tools, devices, apparatuses, etc. Furthermore, by the expensive alkyl silicate and alcohol, the cost of the molded products is raised, and thereby, the demand for the molded products has been being hindered from being expanded.

The water silica sol used in the present invention is a conventional marketed product and does not contain any acid or alcohol at all. So, the pollution of the working environment, any trouble on the health and sanitation of workers, and any trouble on the maintenance of jigs, tools, devices, apparatuses, etc. do not occur at all, and very safe operation is possible. Moreover, the molded products can be produced at a low cost, and hence, the expansion of demand can be greatly expected. Besides, though it was considered that water silica sol could not be controlled in gelling time, the water silica sol can be kept flowable for a certain desired period of time and then rapidly gelled because the gelling time can be controlled.

[Means for solving the problems]

The present invention is a method of producing a gel or a molded product, comprising the step of controlling the ratio of the added amount of the salt (hereinafter called the neutral salt since the aqueous solution of the salt is just about neutral) produced by reaction between a strong base and a strong acid to

the added amount of the salt (hereinafter called the basic salt, because the aqueous solution of the salt is weakly basic)

produced by reaction between a strong base and a weak acid, and also the total amount of the salts used, for gelling water silica sol or a slurry consisting of water silica sol and a granular material after a desired period of time, or molding it in a mold after a desired period of time.

As the group of cations usable as a component of the neutral salt in the present invention, available are  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{++}$ ,  $\text{Ca}^{++}$ ,  $\text{Zn}^{++}$ ,  $\text{NH}_4^+$ , etc., and as the group of anions usable as a component of the neutral salt, available are  $\text{Cl}^-$ ,  $\text{SO}_4^{--}$ ,  $\text{NO}_3^-$ , etc. The neutral salt can be, for example,  $\text{LiCl}$ ,  $\text{NaCl}$ ,  $\text{KNO}_3$ ,  $\text{MgSO}_4$ ,  $\text{Ca}(\text{NO}_3)_2$ ,  $\text{ZnCl}_2$  or  $\text{NH}_4\text{NO}_3$ , etc. The group of cations usable as a component of the basic salt is as enumerated for the neutral salt, and as the group of anions usable as a component of the basic salt, available are  $\text{HSO}_4^{--}$ ,  $\text{CO}_3^{--}$ ,  $\text{CH}_3\text{COO}^-$ ,  $\text{HCOO}^-$ , etc. The basic salt can be, for example,  $\text{Li}_2\text{CO}_3$ ,  $\text{CH}_3\text{COONa}$ ,  $\text{KHSO}_4$ ,  $(\text{CH}_3\text{COO})_2\text{Mg}$ ,  $(\text{CH}_3\text{COO})_2\text{Zn}$  or  $(\text{NH}_4)_2\text{CO}_3$ , etc.

Even if said basic salt is added to weakly basic water silica sol, the water silica sol is not gelled, as far as it is not highly concentrated like a saturated solution and is not excessive in the amount; and a stable sol state is maintained. However, even if a neutral salt is provided as an aqueous solution of about 5 to 10%, if it is added by an amount higher than "a certain level", the water silica sol is thickened and loses its flowability in 2 to 3 minutes, to be very soft gell. However, if the amount of the neutral salt added is lower than "a certain level" even if slightly, the water silica sol remains as a stable sol for a long time, though it is

thickened to some extent. Namely, the water silica sol shows a critical behavior against the amount of the neutral salt added.

Also in the event that the water silica sol is gelled, the viscosity is gradually increased, to lose the flowability, and it does not happen that the water silica sol "keeps flowability for a certain period of time and is then rapidly thickened and gelled". Besides, the time during which the flowability is kept is so short that the control is difficult. Therefore, handling is very difficult, thus being unpractical.

The present invention is a method of producing a gel and a molded product, which enables the gelling time to be controlled as desired within about 20 minutes by adjusting the mixing ratio of at least one or more neutral salts and at least one or more basic salts, and the amount of the mixture (hereinafter called the composite gelling agent) added to the water silica sol.

[Action]

The composite gelling agent used in the present invention is a mixture consisting of a neutral salt with a high gelling capability and a basic salt with a very low gelling capability. The increase of the neutral salt acts to shorten the gelling time, and the increase of the basic salt acts to elongate the gelling time. The increase in the total amount of the salts added acts to shorten the gelling time and to raise the speed from thickening to gelling, and the decrease acts reversely. However, the actions of the present invention are not obtained by the simple combination of high gelling capability and low gelling capability. The detailed mechanism of actions has not been clarified yet, but the gelling time can be controlled by

sufficiently grasping and combining the features of gelling capabilities of the respective salts used.

#### [Effects of the invention]

In the case of the method of producing a gel and a molded product of the present invention, the gelling time can be controlled as desired compared to the conventional method of gelling alcoholic silica sol by the change of pH, and a molded product can be produced using inexpensive materials. Namely, it has another advantage such as to be inexpensive. Compared to the conventional method of adjusting the gelling time by simply adjusting the amount of the gelling agent added, it is an excellent feature of the present invention that the gelling time can be controlled as desired by sufficiently recognizing the actions and effects of the respective salts used and by combining the respective factors.

#### [Examples]

The present invention is described below concretely based on examples, but is not limited thereto or thereby.

##### Example 1

A neutral salt (expressed as N-1 in the table, a 10% KCL aqueous-solution) and a basic salt (expressed as B-1, a 10%  $\text{CH}_3\text{COOK}$  aqueous-solution) were put in a beaker, and sufficiently shaken to obtain a homogeneous (uniform) composite gelling agent. It was put into a beaker containing 20 g of water silica sol (brand name "Snowtex 30" produced by Nissan Chemical Industries, Ltd.), and stirred by a glass rod. The mixture was low in viscosity at first, but a certain period of time later, it was thickened to rapidly lose its viscosity, and gelled. The mixing ratio of the neutral and basic salts, their amount added, and gelling time of each sample are shown in Table 1. For comparison, the

results of a neutral salt alone and a basic salt alone are also shown.

Table 1

Gelling agent		Basic salt B		N + B		Gelling time
Neutral salt N						(minutes)
N-1	4.0g	B-1	2.0g	6g	2g	
"	3.0	"	3.0	6	3	*
"	2.0	"	4.0	6	7	*
"	2.0	"	1.0	4	3	
"	2.0	"	2.0	4	6	*
"	1.0	"	3.0	4	10	*
"	1.5	"	0.5	2	5	
"	1.0	"	1.0	2	10	*
"	0.5	"	1.5	2	15	
"	4.0		0	4	2	
"	3.0		0	3	3 ← A	
"	2.0		0	2	20分以上	20分後でも流動性あり
0		B-1	4.0	4	20分以上	20分後でも流動性あり

A = 20 minutes or more

B = Flowable even after 20 minutes

Example 2

To the five samples marked with \* in Table 1 of Example 1, 75 g. of mixed sand consisting of the same weights of zircon sand and zircon flour was added, to make slurries, and they were cast into 5 x 5 x 1 cm. molds, to obtain molded products. The gelling times and conditions of the molded products are shown in Table 2.





Table 4

Example	Gelling agent			Gelling time (minutes)	Molded product	Remark
	Neutral salt N	Basic salt B	N + B			
3	N-2 3.0 g	B-2 3.0 g	6.0 g	5	ゲル	
4	N-3 3.0	B-4 3.0	6.0	5.5	ゲル	
5	N-5 2.0	B-5 3.0	5.0	6	ゲル	
6	N-4 2.0	B-4 2.0	4.0	5	ゲル	E
7	N-6 0.5	B-6 0.5	1.0	5	ゲル	
8	N-7 0.5	B-8 3.0	3.5	7	ゲル	
9	N-1 0.5	B-1 2.0	2.5	12	ゲル	F
10	N-9 0.5	B-9 2.0	2.5	12	ゲル	
11	N-2 2.0	B-2 2.0	4.0	3	30分後に種内から取出せる	
12	N-3 2.0	B-3 2.0	4.0	3	30分後に種内から取出せる	
13	N-4 2.0	B-4 1.0	3.0	4	30分後に種内から取出せる	
14	N-5 1.0	B-5 1.0	2.0	4	30分後に種内から取出せる	
15	N-6 0.5	B-6 0.5	1.0	4	30分後に種内から取出せる	
16	N-7 0.5	B-7 3.0	3.5	6	30分後に種内から取出せる	
17	N-8 0.5	B-8 3.0	3.5	6	30分後に種内から取出せる	
18	N-2 1.0	B-2 3.0	4.0	7	30分後に種内から取出せる	
19	N-3 1.0	B-3 3.0	4.0	6	30分後に種内から取出せる	
20	N-5 1.0	B-5 2.0	3.0	8	30分後に種内から取出せる	
21	N-6 0.5	B-6 0.5	1.0	8	30分後に種内から取出せる	
22	N-7 0.5	B-7 3.0	3.5	8	30分後に種内から取出せる	
23	N-8 0.5	B-8 3.0	3.5	8	30分後に種内から取出せる	
24	N-1 0.5	B-1 2.0	2.5	12.5	30分後に種内から取出せる	
25	N-2 0.5	B-2 2.0	2.5	15	30分後に種内から取出せる	
26	N-3 0.5	B-3 1.0	1.5	17	30分後に種内から取出せる	

E = Gel only

F = Could be taken out of the mold 30 minutes later.

